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(71) Applicant: **ALCANTARA S.p.A.**
20138 Milano (IT)

(72) Inventors:
- **Costantino, Rocco**
  00157 Roma (IT)
- **Giugliacci, Ennio**
  05100 Terni (IT)
- **Baroni, Elisabetta**
  59100 Prato (IT)
- **Bartolini, Paolo**
  51030 Montale Pistoia (IT)
- **Bartolini, Mario**
  51030 Montale Pistoia (IT)
- **Castagnoli, Massimiliano**
  59100 Prato (IT)
- **Cocci, Mario**
  50041 Calenzano Firenze (IT)

(74) Representative: **Cioni, Carlo**
c/o STUDIO CIONI & PIPPARELLI
Viale Caldara 38
20122 Milano (IT)

(54) Composition for making textile fireproof, procedure for its preparation, and fireproof fabrics treated therewith

(57) Flame-resistant additive for textile materials and particularly for microfiber non-woven fabrics of the artificial-leather type that imparts a high level of fireproofing properties to the textile material treated without negatively affecting the visual and mechanical characteristics, softness to the touch, comprising a mixture of:

a) a fireproofing component constituted by a finely divided mixture of melamine and melamine cyanide and a clay or other adsorbent material such as diatomaceous earth, zeolite, inorganic oxides such as alumina, silica, magnesium oxide or mixtures of inorganic oxides
b) a binder comprising :

- an aqueous dispersion of an acrylic or maleic polymer or copolymer
- a multifunctional cross-linker of the acrylic or maleic polymer or copolymer.

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Description

[0001] The present invention relates to a particularly useful flame-resistant agent for the treatment of non-woven fabrics, a procedure for its preparation and the non-woven fabrics made fireproof by means of treatment with the aforesaid flame-resistant agent. Microfiber non-woven fabrics are known in the art, for instance the type commercialized by ALCANTARA S.p.A.; products of this type are also described in the Italian patents n. 823055, 839921, 858373, 873699, 905222, 921871 and in the patents. US-A-3531368 and US-A-3889292.

[0002] For numerous final applications, for instance furnishing, and in some markets for almost all uses, the microfiber fabrics must conform to precise flame resistance requirements.

[0003] There are essentially three procedures known for endowing microfiber fabrics with the required flame-resistant characteristics. According to a first procedure, known as *padding*, the fabric is subjected to impregnation in a bath containing flame-resistant additives and subsequently dried. This process has the disadvantage of giving a «buffed suede» finish that has worse hand and softness characteristics than the original non flame-resistant product. Furthermore, this treatment is not permanent.

[0004] A second method known as 'back side' coating provides for the application of a paste containing flame-retarding compounds (such as halogens, antimony and phosphorus) to the 'back' side of the synthetic non-woven fabric. This method does not have the disadvantage of *padding* in as much as the right side of the fabric is not affected by the treatment, but given the large quantity of flame-retarding compounds required to confer the desired effect, the treated product presents a «harder» hand and is therefore less drapable than the non-treated product.

[0005] A third method is to form a non-woven fabric compound of intrinsically flame-retardant microfiber polymer (e.g. PET) and a polyurethane solution, which alone or with antimony oxide and deca-bromo-diphenyl oxide additives, impregnates the said substrate.

[0006] Although guaranteeing flame resistance, the combined use of intrinsically fireproof microfiber and additives (in varying proportion to the polyurethane) reflects negatively on the visual appearance (short nap, specking), the drapery (hard hand), and the dyeing characteristics (tone), even though the physical-mechanical performance remains within the required range.

[0007] It is, therefore, desirable to provide a flame-resistant additive for microfiber non-woven fabrics of the synthetic leather type that effectively makes such materials fireproof, without, however, negatively affecting either the physical mechanical characteristics or the aesthetic, hand or dyeing properties of the treated product.

[0008] In the Italian Patent Application NID7AOO 1228 by the same applicant a flame-retarding additive for microfiber non-woven fabric is described, comprising a plurality of microfibers of a polymer material impregnated with a polyurethane matrix, containing trioxide of antimony and deca-bromo-diphenyl oxide that achieves its fireproof activity by means of application on the 'back' side of the fabric, in such quantity and in such form as not to negatively influence the visual and hand characteristics of the material treated. The document quoted above refers to a flame-resistant agent comprising antimony trioxide and deca-bromo-diphenyl oxide in a highly dispersed form and supported on a clay or other adsorbent material such as diatomaceous earth, zeolite, inorganic oxides such as alumina, silica, magnesium oxide or compounds of inorganic oxides.

[0009] The additives described in the aforementioned application and the products treated with the said additives have entered commercial use and satisfy all the specific fireproof properties while maintaining the mechanical and aesthetic properties.

[0010] However, there is a tendency towards ever stricter regulations, that could lead in the future, to the imposition of severe limitations on the use of halogen compounds as components of fireproofing agents.

[0011] The use of antimony derivatives could also be legally restricted in the future, with negative consequences for its wide use as a component of flame-resistant agents.

[0012] A possible alternative to the use of compounds containing bromine and antimony could be the use of phosphorus derivatives for the purpose of identifying compounds able to give fireproof properties to materials impregnated with said compounds.

[0013] However, despite some phosphorus derivatives being known to show fireproof activity, the applicant has not found it possible to identify compounds that simultaneously answer all the requirements established above, when applied to products of the artificial-leather type based substantially on microfiber non-woven fabrics.

[0014] Trials carried out on a large number of compounds containing phosphorus derivatives to determine their suitability as fireproofing agents for materials of the artificial-leather type constituted substantially of microfiber non-woven fabrics, have shown that such additive products, while having good fireproofing characteristics, showed evident aesthetic deficiencies. Another problem posed by the use of phosphorus derivatives as flame-resistant agents is that of identifying a binder that, on one band, allows homogeneous distribution of the additive and yet prevents its separation from the treated product. The separation of the additive from the material treated is commonly called «powdering».

[0015] As far as the properties related to the visual appearance of the product are concerned, it has been verified that the application of flame-resistant compounds imparted a damp or even wet appearance to the product.

[0016] In the Italian Patent Application N1198A00192 of September 4, 1998 the Applicant has proposed the use of a flame-resistant additive for non-woven fabrics consisting of a water-soluble compound of cyclical organic phosphonate complexes, with a phosphorus content between 15% and 20%, and a water-soluble organic polymer.

[0017] Such additive, while conferring excellent fireproofing characteristics on the products treated that remain even after repeated dry cleaning, showed the formation of stains on the fabric when the latter was subjected to the action of the water.

[0018] Therefore the problem of making textile materials and microfiber non-woven fabrics in particular, fireproof in an effective and stable way without influencing the characteristics of the product substantially or negatively, have still not been completely resolved. Therefore, it is a primary purpose of the present invention to provide a flame-resistant additive for microfiber non-woven fabrics of the artificial-leather type that do not contain halogen compounds or other products potentially harmful and impart good fireproof properties to the non-woven fabric without negatively affecting mechanical characteristics or softness to the touch, and without modifying the external appearance even following repeated washings.

[0019] A second purpose of the present invention is a procedure for making microfiber non-woven fabric of the artificial-leather type fireproof by means of the application of the aforementioned flame-resistant additive.

[0020] A third purpose of the invention is a procedure for the preparation of said flame-resistant agent.

[0021] Under another aspect, the invention also relates to microfiber non-woven fabrics made fireproof by the aforementioned treatment.

[0022] These objectives are achieved by the present invention through the provision of a fireproofing additive for textile products and particularly for microfiber non-woven fabrics of the artificial-leather type

a) a fireproofing component consisting of a finely divided compound of melamine and melamine cyanide and a clay or other adsorbent material such as diatomaceous earth, zeolite, inorganic oxides such as alumina, silica, magnesium oxide or compounds of inorganic oxides
b) a binder consisting of

- an aqueous dispersion of an acrylic or maleic polymer or copolymer
- a multi-functional cross-linker of the acrylic or maleic polymer or copolymer.

[0023] It is known that melamine and its derivatives constitute a class of materials which impart flame-resistant characteristics to polymer materials. However, these fireproof characteristics are generally conferred by modifying the polymer, i.e. the melamine or the melamine derivative are mixed intimately with the polymer prior to molding of the same in such a way as to get, after working (extrusion, molding, pressure die-casting), a product with intrinsic flame-resistant characteristics. As has been said at the beginning, this polymer fireproofing procedure in which the polymer is directly linked to the fireproofing functional group or molecule gives a product that, when made up into textile materials, has characteristics clearly inferior to those of the original untreated polymer. This variation of properties of the formed polymer is particularly important in the case of delicate textile products like, for instance, microfiber non-woven fabrics of the artificial-leather type.

[0024] On the other hand, simple impregnation with fireproofing additive of the finished textile material to be fireproofed doesn't guarantee the maintenance of the properties of the material after repeated dry cleaning or washing with water, in as far as the fireproofing agent is progressively removed from the surface of the textile material.

[0025] In the additive according to the invention, the fireproofing agent constituted by the melamine and melamine cyanide mixture is not removed, even when subjected to repeated washings in severe conditions, because it is entrapped in the acrylic or maleic copolymer as a result of the crosslinking caused by the same multifunctional aziridine binder.

[0026] The fireproofing component according to the invention is in the form of a suspension of particles whose average size is less than 10□, preferably between 1 and 5□ and contains from 0.05% to 5% by weight of a clay or other adsorbent material chosen from diatomaceous earth, zeolite, inorganic oxides such as alumina, silica, magnesium oxide or a mixture of inorganic oxides. The fireproofing component of the present invention is obtained by mixing the components already reduced to the desired granule size or the said granule value could be obtained by grinding the mixture of the ingredients.

[0027] The additive could be applied to the textile material, particularly to non-woven fabric, by the traditional type of application: coating by knife spreader. However, particularly advantageous results have been obtained with a coating treatment referred to as 'transfer roller' coating, which consists in releasing an amount of application additive carried over from a roller, from the lower part toward the top onto the 'back' face of the material, as described in the of Italian Patent Application N4197A001228.

[0028] The fireproofing component could comprise other products that impart other desired characteristics or that favor the formation and the stabilization of the suspension and the application to the textile material. Products of this

type are surfactants, dispersants, wetting agents, pH buffers, anti-fermenting agents and similar agents.

[0029] The melamine or melamine cyanide content in the fireproofing component varies between 30% and 90% of the total, while the ratio by weight of melamine to melamine cyanide could vary between 0,01: 1 and 0,5: 1.

[0030] The binder comprises an acrylic copolymer or polymer that has free carboxyl or ester groups and preferably could be any of the polymers or copolymers of acrylic or metacrylic acid or its esters or salts, or of the maleic anhydride polymers or copolymers. Particularly good results have been obtained with the copolymer of acrylic acid or its derivatives and styrene.

[0031] The term «binder» also covers a cross-linking agent that has a critical function for the achievement of the invention. The cross-linking agent must react with the acrylic polymers and copolymers of the binder to give a three-dimensional structure inside of which is imprisoned the fireproofing component. The cross-linking agent must also cause the formation of some forms of bond between the three-dimensional structure and the surface of the textile material being fireproofed. Furthermore, the cross-linking should of necessity happen quickly and at temperatures compatible with the stability of the textile material being treated.

[0032] Multifunctional derivatives of aziridine have shown themselves particularly useful cross-linking agents and fulfill the aforesaid requirements. Multifunctional derivatives of aziridine refers to compounds that beyond the imine group of aziridine have other imine or amine groups that can react with the carboxyl groups of the acrylic polymers or copolymers or of the maleic anhydride polymers or copolymers to form stable bonds.

[0033] Among the multifunctional aziridines useful in binding the fireproofing additive of the present invention are N-(aminoethyl)-aziridine, N-aminoethyl-N-aziridyl ethylamine, N, N-bis-2-aminopropyl-N-aziridylethylamine.

[0034] The proportion of cross-linking agent to polymer binder depends on the structure of the agent cross-linking and varies between 0.5% and 5% by weight.

[0035] The binder and the cross-linking agent are added and mixed into the fireproofing component at the moment of application to the textile material and the product being treated for fireproofing is subjected to heating to dry the product and ensure the cross-linking of the binder. Binder is added to the fireproofing component in quantities from 1% at 30% by weight of the same fireproofing component.

[0036] The components a) and b) of the flame-resistant additive according to the present invention are produced by the SUPER GLANZ company under the commercial names of CABERTEX CLA 200 (component a) and ACR-EF Stiffener and catalyst (component b).

[0037] The flame-resistant additive according to the present invention consists, as stated above, of a concentrated aqueous solution with a high specific gravity between 1.05 and 1.25, and a viscosity between 80 and 300 cps at 23±2□C.

[0038] The quantity of flame-resistant additive according to the invention, necessary to make the non-woven fabric material fireproof, is appreciably less than that of conventional flame-resistant additives to give the same degree of fireproofing. The said quantity varies between 15% and 60% by weight of the material to be treated, and is preferably between 20% and 40%. It is believed that the high degree of subdivision of the flame-resistant additive according to the invention, in addition to the dispersing and deflocculant action of the adsorbent support, favors the penetration of the fabric by the same, so improving the fireproof characteristics.

[0039] Preferably, the flame-resistant composition according to the present invention is prepared directly at the moment of use or immediately beforehand to limit storage problems.

[0040] The examples that follow illustrate the advantages of the invention; they are by way of example and should in no way be considered as limiting its scope.

[0041] The characteristics of non-woven fabric materials comprising the flame-resistant additive according to the invention are shown in the attached chart where they are compared with those of the same non-woven fabric materials treated with flame-resistant additives not coming within the ambit of the present invention.

[0042] The quantity of flame-resistant additive according to the invention necessary to make the non-woven fabric material fireproof is appreciably less than that of conventional flame-resistant additive needed to give the same degree of fireproofing.

[0043] The said quantity could vary between 15% and 60% by weight of the material to be treated, and preferably between 20% and 40%. It is believed that the homogeneous mixture of the components, characteristic of the composition of the additive according to the invention, allows uniform dispersion of the product and favors the penetration of the fabric by the same, so improving the fireproof characteristics.

[0044] It should be noted that the principal characteristic of the additive according to the invention is that it can be used in large quantities, therefore imparting a high level of flame-resistance to the materials treated, without reducing the aesthetics and softness to the touch of the product.

[0045] The fine subdivision of the additive improves the adherence of the same to the material to be treated and that makes possible products that don't show «powdering» phenomena i.e. the separation of the additive.

[0046] While the flame-resistant additive according to the invention could be used to impart fireproofing properties to any type of textile material, its use is, however, particularly advantageous in the field of materials constituted by

microfiber non-woven fabrics.

[0047] The procedure of application of the additive to the non-woven fabric material could be of traditional type to coating by knife spreader. However, it has been found that particularly advantageous results can be obtained with a coating treatment (called «transfer roller «) where a roller partially immersed in the suspension of the additive according to the invention, transfers the suspension of additive from the lower part toward the top onto the 'back' face of the material. The regulation of the distance of a shaving roller allows the desired dose quantity of additive to be carried over onto the transfer roller. The procedure of application of a flame-resistant material to a microfiber non-woven fabric and an apparatus comprising the transfer roller is described in the enclosed Italian Patent Application M197A001228 of the same applicant.

[0048] The examples that follow illustrate the advantages achieved with the application of the fireproofing additive according to the invention on varied types of materials. Such examples are by way of illustration only and do not restrict the scope of the present invention.

[0049] The resistance to combustion and speed of combustion trials have been carried out on samples of microfiber non-woven fabric, and on composite material - the same materials joined with cotton cloth and polyester cloth, with fireproofed cloths, with foams.

[0050] The application of the additive was performed by dispersing the additive, constituted by the fireproofing component and the binder comprising the copolymer and the cross-linking agent, in water. The quantity of additive spread was such as to give the desired quantity of additive (after drying and cross-linking) in the final dry product.

[0051] The criteria and methods of evaluation of the trials of the treated materials are indicated below:

Hand

[0052] Evaluated on a scale of 1 to 5, where 5 is the maximum and 1 is the vote assigned to the material that had worst softness.

Cohesion

[0053] Determined by the UNI 481810 method and giving results inclusive between 5 and 15 Newton.

Fire Resistance

[0054] Determined by the RF1 method and consists of determining the post-combustion time and of post-incandescence time, the damaged zone and the dripping of a test-piece stretched and suspended vertically with a U-shaped support, whose lower free edge was exposed to a flame according to CSE RF 1/751A standard.

[0055] The products evaluated were divided into categories starting from **1A** (high resistance to fire).

FMVSS302 (speed of combustion)

[0056] It is expressed in millimeters per minute (mm/min.) and was determined with the FMVSS 302 method that consists of determining the speed of combustion, according to the UNI - ISO 3795 standard of a test-piece stretched horizontally on a U-shaped frame, whose free edge is exposed to a flame of modest energy. The speed of propagation was determined both on the material thus treated and on the same material after it had been subjected to dry cleaning and washing with soap and water.

[0057] The results of the trials are shown on chart A below in which the data obtained are the average of evaluations of different non-woven fabrics materials, either microfiber alone or composite with support, treated with equivalent quantities of flame-resistant additive.

[0058] As can be seen from the chart, the treatment of the composite material, microfiber, non-woven fabric with the additive according to the invention, beyond influencing in less measure the properties of the product, imparts better flame-resistance for equal quantities of additive applied.

[0059] In the chart the products have the followings meanings:

PANNEL:	Non-woven fabric
COMPACT:	Non-woven fabric composite
CABERTEX CLA:	Additive comprising melamine, melamine cyanide, dispersants, wetting agents, suspending media, pH buffers, clay and anti-fermentation agents (SUPER GLANZ product)

CABERTEX CLA 200	Additive with the same composition as Cabertex CLA with granule size <5 micron (obtainable from SUPER GLANZ)
ACR EF Stiffener	Aqueous dispersion of copolymer acrylic styrene (SUPER GLANZ product)
CROSSLINKER:	Polyfunctional aziridine (obtainable from SUPER GLANZ)
COAT THICKNESS:	Distance in mm between the transfer roller and the coating roller
ROLLER TOLERANCE:	Distance in mm between the coating roller and the pressure roller
WATER STAIN:	Stain formation following treatment with water and drying

DISPERSANT DRY RESIDUE% of product after elimination of water

Trial	no.	1	2	3	4	5	6	7	8	9	10	11	12	13a	13b	14a	141	15a	15b	15c
Cabertex CLA	%	80	80	80	60	60	70	-	-	-										
Cabertex CLA 2OO	%							80	80	77	67	70	72	72	72	72	72	72	72	72
ACR-EF Stiffener	%		20	20	25	25	30	20	20	23	24	20	18	18	18	15	15	16	16	16
Water	%				15	15	2		2	2	9	10	10	10	10	13	13	12	12	12
Crosslinker	%			2	2	2	2		2	2	1	1	1	1	1	1	1	1	1	1
Dispersant dry residue.	%	23									40			39		40		41		
Roller separation	mm									0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.25	0.10	0.20	0.30
Roller tolerance	mm									0.70	0.75	0.75	0.70	0.55	0.70	0.70	0.70	0.70	0.70	0.70
Dry residue per piece	%	--	23	20	16	15	17	30	35	25	24	23	23	24	22	32	30	24	25	28
FMYSS3O2/ pannel	Mm damage				0–253	253	0–253	–	0–115	0–253	0–80	0–65	0–253	0–90	0–90	0–253	0–90	0–253	0–253	0–253
	speed of prop.				180	150	170	--	95	70/150	30/100	90	30	70	70	35	35	35	35	35
FMVSS3O2 after 3 soap washes	mm damage																	0–70	0–70	0–70
	speed of prop.																	70	70	70
RF1	category													1st-3rd	1st-3rd			1st-3rd	1st-3rd	1st-3rd
Hand	-	2	2	2	2	2–3	2–3	--	3	3	3	3	3	3	3	3	3	3	3	3
FMVSS3O2 after 3 dry cleanings	mm damage																	0–130	0–130	0–130
	speed of prop.																	65	65	65
Water stain	visible								no	no	no	no	no	no	no	no	no	no	no	no
Cohesion	Newton								5	9			5					9	8	9
FMVSS3O2 / compact	mm damage								<253				<253	<253	<253			<253	<253	<253
	speed of prop.								<95				<50	<80	<70			<55	<55	<55

Claims

1. Flame-resistant additive for textile materials and particularly for microfiber non-woven fabrics of the artificial-leather type that imparts a high level of fireproofing properties to the textile material treated without negatively affecting the visual and mechanical characteristics, softness to the touch, characterized by comprising a mixture of:

   a) a fireproofing component constituted by a finely divided mixture of melamine and melamine cyanide and a clay or other adsorbent material such as diatomaceous earth, zeolite, inorganic oxides such as alumina, silica, magnesium oxide or mixtures of inorganic oxides
   b) a binder comprising:

   - an aqueous dispersion of an acrylic or maleic polymer or copolymer
   - a multifunctional cross-linker of the acrylic or maleic polymer or copolymer.

2. Flame-resistant additive for textile materials according to Claim 1, characterized by the binder comprising preferably an acrylic copolymer or polymer that has free carboxyl or ester groups and is chosen from among the polymers and copolymers of acrylic or metacrylic acid or its esters or salts, and between the polymers and copolymer of maleic anhydride.

3. Flame-resistant additive for textile materials according to Claim 2, characterized by the binder comprising a copolymer of styrene and acrylic acid.

4. Flame-resistant additive for textile materials according to Claims from 1 to 3, characterized by the cross-linking agent being a multifunctional aziridine derivative.

5. Flame-resistant additive for textile materials according to Claims from 1 to 3, characterized by the cross-linking agent being chosen from among N-(aminoethyl) aziridine, N-aminoethyl-N-aziridyl ethylamine, N, N-bis-2-aminopropyl-N-aziridylethylamine.

6. Flame-resistant additive for textile materials according to Claims from 1 to 4, characterized by the fireproofing component being in the form of a suspension of particles whose average size is less than 10□, preferably between 1 □ and 5□, and containing from 0.05% to 5 % by weight of a clay or other adsorbent material chosen from diatomaceous earth, zeolite, inorganic oxides such as alumina, silica, magnesium oxide or mixtures of inorganic oxides.

7. Flame-resistant additive for textile materials according to Claims from 1 to 6, characterized by the fireproofing component containing surfactants, dispersants, wetting agents, pH buffers, and anti-fermentation agents.

8. Flame-resistant additive for textile materials according to one or more of the preceding claims characterized by the relationship between melamine and melamine cyanide in the component fireproof being inclusive between 0,01: 1 and 0,5:1.

9. Flame-resistant additive for textile materials according to one or more of the preceding claims characterized by the quantity of melamine and melamine cyanide in the fireproof component being inclusive between 30% and 90% of the total.

10. Procedure for making textile materials fireproof characterized by the textile material being treated with an additive comprising:

    a) a fireproofing component constituted by a finely divided mixture of melamine and melamine cyanide and a clay or other adsorbent material such as diatomaceous earth, zeolite, inorganic oxides like alumina, silica, magnesium oxide.or mixtures of inorganic oxides
    b) a binder comprising

    - an aqueous dispersion of an acrylic or maleic polymer or copolymer.
    - a multifunctional cross-linker of the acrylic or maleic or copolymer.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 11 3138

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	WO 98 27164 A (BASF AG ;WEBER WILHELM (DE); DECKERS ANDREAS (DE); KLATT MARTIN (D) 25 June 1998 (1998-06-25) * page 20, line 42 - page 21, line 31 * * example 7 * * claim 6 *	1-10	D06M13/364 D06M13/358 D06M11/00 D06M15/263
A	EP 0 718 388 A (BALLE ERIKA ;OTTO EUGEN (DE); OTTO UTA DR (DE)) 26 June 1996 (1996-06-26) * page 4, line 54 - page 5, line 12 * * claims 8-14 *	1-10	
A	GB 1 480 556 A (TORAY INDUSTRIES) 20 July 1977 (1977-07-20) * page 1, line 9 - line 41 *	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

D06M
D01F
C09K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 October 2000	Fiocco, M

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 11 3138

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82